Journal of Physics: Condensed Matter

PAPER • **OPEN ACCESS**

Stability predictions of magnetic M_2AX compounds

To cite this article: Dominik Ohmer *et al* 2019 *J. Phys.: Condens. Matter* **31** 405902

OPEN ACCESS
IOP Publishing
Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **31** (2019) 405902 (6pp)
https://doi.org/10.1088/1361-648X/ab2bd1

Stability predictions of magnetic M_2AX compounds

Dominik Ohmer, Ingo Opahle, Harish K Singh and Hongbin Zhang

Department of Materials Science, Technische Universität Darmstadt, Darmstadt, Germany

E-mail: hzhang@tmm.tu-darmstadt.de

Received 18 March 2019, revised 20 May 2019
Accepted for publication 21 June 2019
Published 15 July 2019

Abstract

Based on high throughput density functional theory calculations, we evaluated systematically the stability of 580 M_2AX compounds. The thermodynamic, mechanical, and dynamical stability and the magnetic structure are calculated. We found 20 compounds fulfilling all three stability criteria, confirming Cr_2AlC, Cr_2GeC, Cr_2GaC, Cr_2GaN, and Mn_2GaC, which have been synthesized. The stability trends with respect to the M- and A-elements are discussed by analyzing the formation energies, indicating that Cr and Mn containing M_2AX compounds are more stable than Fe, Co, or Ni containing compounds. Further insights on the stability are obtained by detailed analysis of the crystal orbital Hamilton population (COHP).

Keywords: MAX phase, DFT, high-throughput, stability calculations

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Due to the their unique combination of metallic and ceramic properties, *MAX* phases have attracted significant attention since the 1990s, when Barsoum investigated the mechanical properties of Ti_3SiC_2 [1]. In general, they are ternary compounds with the chemical formula $M_{n+1}AX_n$ ($n = 1, 2, 3$), with M being an early transition metal, A being an A-group element, and X being C or N. Despite their discovery in the 1960s by Nowotny [2], the synthesis of new *MAX* phases and new synthesis routes are current topics for material scientists and chemists, e.g. via microwave sintering [3] or possible directional diffusion of C/N [4]. For example, Zr_2AlC has recently been synthesized by Lapauw [5], followed by a number of Zr- and Al-containing solid solutions. [6, 7] Non-conventional synthesis routes for the magnetic *MAX* phases $(Cr/Mn)_2AlC$ and $(Cr/Fe)_2AlC$ are carried out by Hamm [8], using microwave heating and spark plasma sintering.

Beside the mechanical properties, magnetic *MAX* compounds are of particular interest due to their nanolaminated structure, where M_2X layers are sandwiched between A layers (figure 1). Several magnetic *MAX* phases have been synthesized, such as $(Cr_{0.75}Mn_{0.25})_2GeC$ [9], $(Cr_{1-x}Mn_x)_2AlC$ [10, 11], and $(Cr_{1-x}Mn_x)_2GaC$ [12].

Ingason synthesized the first magnetic *MAX* compound which has only one M-element, namely Mn_2GaC [13]. From the theoretical point of view, the stability of magnetic *MAX* phases has been investigated using the first-principles approach by Dahlqvist [14, 15]. It was suggested that maximum stability occurs for V and Ti as transition metal for C and N containing *MAX* phases, respectively. Aryal [16] performed density functional theory (DFT) calculations on almost 800 *MAX* phases and suggested that around 600 are at least thermodynamically and mechanical stable, but only based on the calculation of the formation energy.

In this work, high throughput screening for new magnetic *MAX* compounds of the M_2AX type has been performed. Starting from 580 systems where Cr, Mn, Fe, Ni, and Co are considered as M, C and N as X, and the A-element is systematically varied from Li to Bi (except for the inert gas and B, C, N, O, and F), we obtain 20 stable *MAX* compounds based on systematic evaluation of the thermodynamic, mechanical,

and dynamic stabilities. It is observed that both ferromagnetic and antiferromagnetic configurations can be realized based on explicit comparison of the total energies. Detailed analysis of the crystal orbital Hamilton population (COHP) is used to compare the chemical bonds of the newly predicted compounds with the synthesized ones. Similar chemical structures are found for six compounds, of which Cr_2GeN, Mn_2AlC, and Mn_2GeC are calculated to be magnetic in their ground state.

2. Numerical details

The calculations are based on DFT as implemented in the Vienna *ab initio* simulation package (VASP) [17, 18], using the projector-augmented wave (PAW) method [19]. As introduced in our previous work [20], the high-throughput environment (HTE) [21, 22] is used to generate the *VASP* input files. This is followed by a two-step structure optimization: A first optimization is performed on the non-magnetic configuration using the ultrasoft pseudopotentials (US-PP) [23, 24] in combination with the parameterization of the exchange-correlation functional according to the PW91 formalism [25]. The cutoff energy is set to 250 eV with a k-space density of 30 (product of the number of k-points and the length of lattice constant in Å). For final structure optimization, the PAW method and the generalized gradient approximation (GGA) [26, 27] after Perdew, Burke, and Ernzherhof (PBE) [28] are used with a cutoff energy of 350 eV and a k-space density of 40. These values are chosen to guarantee good convergence.

In order to evaluate the thermodynamic stabilities including both the formation energy and the distance to the convex hull, the total energies for the magnetic ground states are calculated. The elastic constants (as done for TiO_2 [29]) and phonon dispersion spectra are calculated using the optimized structures with the magnetic ground state configuration as well. The thermodynamic, mechanical, and dynamical stability criteria are introduced in detail in [30]. The phonon disperion spectra are obtained using *Phonopy* [31], where the force constant matrices are calculated by *VASP*, based on the density functional perturbation theory (DFPT). $2 \times 2 \times 1$ supercells and $8 \times 8 \times 2$ Γ-centered k-meshes are used in combination with a cutoff energy of 550 eV and a smearing width of 0.6 eV to achieve convergence. The crystal orbital Hamilton population (COHP) calculations are performed using the local-orbital basis suite towards electronic-structure reconstruction (*LOBSTER*) code [32].

3. Results and discussion

As shown in table 1, we found that there are 20 compounds which satisfy the thermodynamic (including the formation energy and convex hull), mechanical, and dynamic stability. Five of the 20 compounds have already been synthesized. Cr_2AlC, Cr_2GaC, and Cr_2GeC have been synthesized both as bulk and thin films, using hot isostatic pressing (HIP) or solid state reactions for the bulk samples and magnetron sputtering for the thin films [12, 33–38]. Cr_2GaN has been synthesized in bulk [35] and Mn_2GaC has been synthesized as a thin film [13, 39]. Thus, we predict 15 new magnetic *MAX* compounds which are promising for further experimental exploration. It is observed that the distance to the convex hull plays a significant role in the number of resulting stable compounds. For instance, 165 out of the 580 calculated compounds have negative formation energies (see table S1 (stacks.iop.org/JPhysCM/31/405902/mmedia)), while only 25 are within the 50 meV/atom tolerance for the convex hull. Furthermore, we find that Mn_2ClC is mechanically unstable and Cr_2ClC, Cr_2PtC, Mn_2ClN, and Mn_2GeN are dynamically unstable, reducing the number of stable magnetic systems to 20. The five mechanically or dynamically unstable compounds may still be synthesized under nonequilibrium conditions, e.g. using the molecular beam epitaxy method.

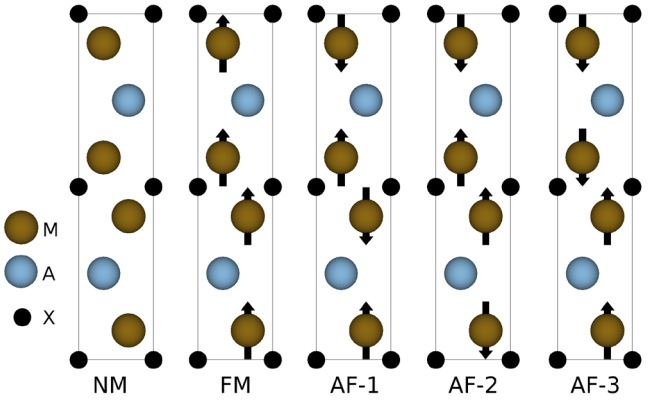

Figure 1. Magnetic configurations within magnetic *MAX* compounds.

The 20 stable compounds either have Cr or Mn as the magnetic element. There is no stable magnetic *MAX* compound with Fe, Co or Ni on the M-site. Closest to the convex hull are Fe_2ZnC, Co_2ZnC and Ni_2PtN with a distance of 42, 58 and 127 meV/atom, respectively. Fe_2ZnC is less than 50 meV/atom above the convex hull, but has a positive formation energy and is therefore excluded from table 1 as this indicates instability against the decomposition into the elements. While this does not exclude the formation of a compound, taking into account finite temperature effects or errors due to GGA, our results indicate that a synthesis of M_2AX compounds with M = Co or Ni is unlikely under equilibrium conditions.

The magnetic ground states are obtained by comparing the total energies of the different magnetic configurations shown in figure 1. Seven compounds are calculated to be ferromagnetic, seven compounds are found to be anti-ferromagnetic and six converged to the non-magnetic state. The non-magnetic compounds all have Cr as M-element. Cr_2GeN and Cr_2GaN are the only Cr-containing compounds that are not calculated to be non-magnetic. Instead, their magnetic ground state is calculated to be the AF-3 configuration with the Cr-atoms exhibiting magnetic moments of 1.51 and 1.47 μ_B in Cr_2GaN and Cr_2GeN, respectively. The largest magnetic moments are found in the Mn-containing compounds, ranging between 1.8 μ_B in the anti-ferromagnetic Mn_2GeC and 2.62 μ_B in the ferromagnetic Mn_2PdN. From these observations, we

Table 1. The calculated formation energies E_f and distances to the convex hull dE_{CHULL} in eV/atom of the 20 stable magnetic *MAX* compounds are shown together with the total energy differences in eV/atom between the magnetic ground state (GS) and the other magnetic configurations. Compounds are considered stable, when E_f is negative and dE_{CHULL} is smaller than 50 eV/atom. The corresponding magnetic ground state and magnetic moment μ_M of the M-atoms in μ_B/atom are also shown. The compounds in bold have been synthesized.

MAX	E_f	dE_{CHULL}	ΔE_{NM}	ΔE_{FM}	ΔE_{AF-1}	ΔE_{AF-2}	ΔE_{AF-3}	GS	μ_M
Cr_2AlC	**− 0.1688**	**0.0000**	**0**	**—**	**—**	**—**	**—**	**NM**	**0.00**
Cr_2GaC	**− 0.1319**	**0.0000**	**0**	**—**	**—**	**—**	**—**	**NM**	**0.00**
Cr_2GaN	**− 0.4090**	**0.0240**	**0.0233**	**0.0152**	**0.0244**	**0.0244**	**0.0000**	**AF-3**	**1.51**
Cr_2GeC	**− 0.0752**	**0.0110**	**0**	**0.0002**	**—**	**—**	**—**	**NM**	**0.00**
Cr_2GeN	−0.3525	0.0380	0.0248	0.0186	0.0047	0.0248	0	AF-3	1.47
Cr_2IrC	−0.1215	0.0240	0	—	—	—	—	NM	0.00
Cr_2OsC	−0.0506	0.0300	0	—	—	—	—	NM	0.00
Cr_2RhC	−0.0701	0.0410	0	—	—	—	—	NM	0.00
Mn_2AlC	−0.1811	0.0030	0.0786	0	0.0073	0.0405	0.0154	FM	1.86
Mn_2AuN	−0.2836	0.0460	0.1611	0	0.0077	0.0082	0.0088	FM	2.43
Mn_2GaC	**− 0.1514**	**0.0000**	**0.0995**	**0**	**0.0418**	**0.0017**	**0.0212**	**FM**	**1.94**
Mn_2GaN	−0.3976	0.0370	0.0891	0.0321	0	0.0181	0.0392	AF-1	2.00
Mn_2GeC	−0.0923	0.0000	0.0955	0.0146	0	0.0047	0.0306	AF-1	1.80
Mn_2IrC	−0.0666	0.0450	0.1323	0.0171	0.0329	0	0.0423	AF-2	2.33
Mn_2IrN	−0.3530	0.0000	0.1702	0.0094	0.0294	0	0.0338	AF-2	2.42
Mn_2PdN	−0.3237	0.0480	0.1795	0	0.0148	0.0102	0.0046	FM	2.62
Mn_2PtN	−0.4014	0.0140	0.2415	0	0.0150	0.0011	0.0197	FM	2.51
Mn_2RhN	−0.3204	0.0100	0.1792	0	0.0243	0.0000	0.0272	AF-2	2.49
Mn_2ZnC	−0.0597	0.0020	0.1039	0	0.0248	0.0828	0.0539	FM	2.18
Mn_2ZnN	−0.3142	0.0050	0.1181	0	0.0146	0.0385	0.0153	FM	2.12

state that the interlayer magnetic coupling tends to be ferromagnetic, while the intralayer coupling can either be ferro- or anti-ferromagnetic.

To show the importance of considering the correct ground state for the investigation of the stability, we present the absolute energy differences between the magnetic ground state and the considered magnetic configurations in table 1. At this point, we mention that there are more possible anti-ferromagnetic configurations, e.g. in-plane ordering and long-ranged AFM as considered in [40], but their calculation requires larger supercells and therefore significantly more computational effort. In [41], the magnetic ground state of Mn_2GaC is shown to be AFM with a magnetic repetition distance of two unit cells. However, according to Novoselova *et al* [42] Mn_2GaC exhibits a non-collinear AFM state below 214 K and undergoes a first order transition to collinear AFM. The non-collinear AFM is considered to be a result of the competition between AFM and FM ordering. As can be seen in table 1, the energies for AFM and FM ordering differ only by 0.0017 eV/atom.

We observe, that the energy differences between the non-magnetic and the ferro- or anti-ferromagnetic configurations are the largest with up to 250 meV per atom. The energy differences between ferro- and anti-ferromagnetic configurations are smaller but with up to 83 meV per atom, e.g. for Mn_2ZnN, the differences are significant. With respect to the investigation of the thermodynamic stability, these energy differences are large enough to shift possibly stable compounds above the convex hull when the wrong ground state is considered. Only performing non-magnetic calculations, Mn_2IrC and Mn_2GaN would not be listed stable above, as their distance to the convex hull is 62 and 69 meV per atom in the non-magnetic state, respectively. Another example for the importance of the correct ground state is Mn_2GeC. In the ferromagnetic state, Mn_2GeC is calculated to be 14 meV above the convex hull. However, considering the AF-1 configuration, Mn_2GeC is calculated to be on the convex hull as the energy difference between the two configurations is 14.58 meV. We therefore emphasize that only performing non-magnetic or ferromagnetic calculations is not enough to predict the stability of these compounds. Further, an anti-ferromagnetic ground state may lower the energy of the competing phases, which is not considered in our calculations and may have an impact on the calculated phase stability.

In order to discuss stability trends with respect to the variation of M and A, we plot the formation energies for Cr, Mn, Fe, Co, and Ni as M with respect to the considered A-elements of the fourth, fifth, and sixth period in figures 2(a)–(c). We observe for the variation of M, that the trends are similar for all five elements, but from Cr to Ni the formation energies increase, indicating higher stability for Cr and Mn containing *MAX* compounds. This is in agreement with the results presented before, as we do not obtain any Co or Ni containing compounds within a distance of 50 meV/atom to the convex hull.

For the variation of the A-element within the fourth period (figure 2(a)), we observe a minimum of the formation energies for Ga on the A-site. In general, the formation energies

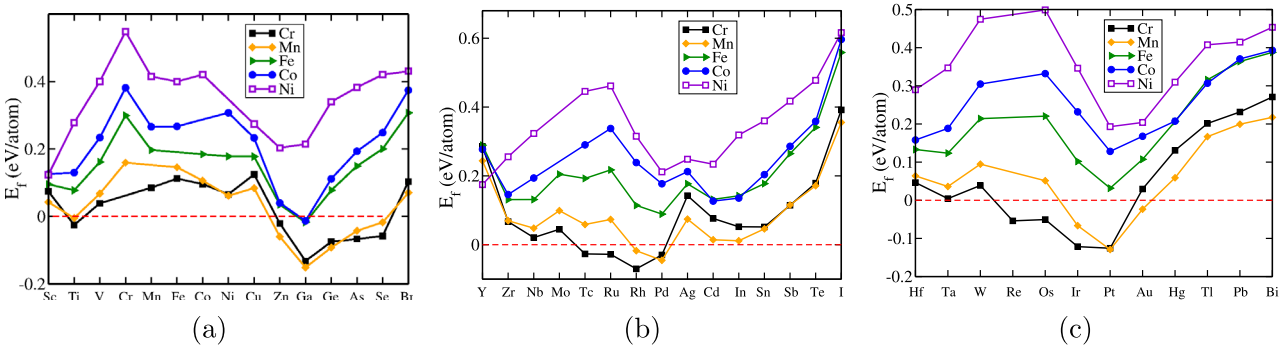

Figure 2. Formation energies for M_2AX with M = Cr, Mn, Fe, Co, and Ni and X = C with respect to the A-element. The A-element is varied through the (a) fourth, (b) fifth, and (c) sixth period of the periodic table.

are lower for A-group elements as A compared to *3d*-transition metals. Only for Ti and Zn we obtain negative formation energies.

In contrast to this, we do not observe negative formation energies for A-group elements of the fifth or sixth period as A-element. For the fifth and sixth period, we obtain a minimum of the formation energy around Rh and Pt, respectively. The formation energies of *MAX* compounds with *4d*- and *5d*-transition metals on the A-site are lower than with A-group elements of the same period. Negative formation energies are obtained for Tc, Ru, Rh, and Pd for the variation within the fifth period and for Re, Os, Ir, Pt, and Au for the variation within the sixth period.

From these observations we conclude that a synthesis of new magnetic *MAX* compounds with *4d*- and *5d*-transition metals on the A-site is an attractive alternative to the synthesis with A-group elements. This is supported by the work of Lai *et al* [43], in which Ga is partially substituted by Fe in Mo_2GaC. Even though this is only achieved by using Au as a catalyst for the chemical reaction, it shows that *MAX* compounds with transition metals on the A-site can in principal be synthesized. Further, it is worth mentioning that for alkali and alkaline earth metals we did not find any compound on the convex hull or less than 50 meV/atom above. For these compounds, the smallest distance to the convex hull was found in Mn_2MgC with 79 meV/atom. We therefore conclude that magnetic *MAX* compounds with alkali or alkaline earth metals are unstable.

Since we aim for reliable predictions of new magnetic MAX compounds, we investigate the synthesized *MAX* phases Cr_2AlC, Cr_2GaN, Cr_2GaC, Mn_2GaC, and Cr_2GeC in more detail to understand their stability and compare them to the other compounds in table 1 by analyzing the COHP. In figure 3, the COHP of the M–X (red) and M–A (black) bonds are plotted for the five synthesized compounds in their calculated ground state according to table 1.

It can be seen that only bonding orbitals are occupied within the M–A bonds. In addition, there is no occupation of anti-bonding orbitals in the M–X bonds of Cr_2AlC, Cr_2GaC, and Cr_2GeC. For the synthesized compounds, occupied anti-bonding states can only be observed in the M–X bonds of Cr_2GaN and Mn_2GaC, for which the COHP is negative at the Fermi energy. Although anti-bonding states are occupied in

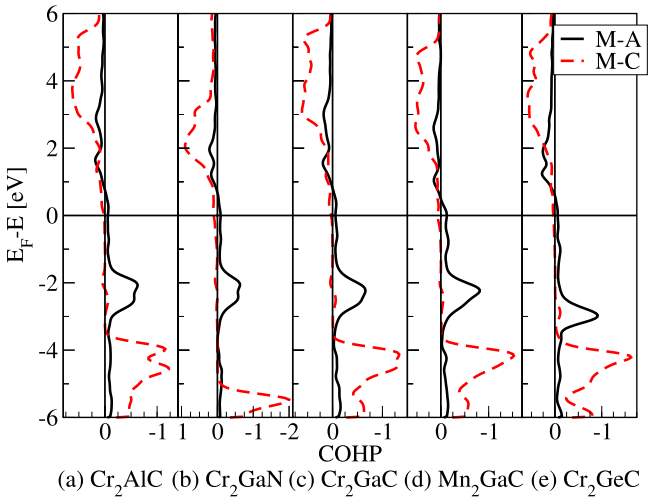

Figure 3. COHP of the M–A and M–X (dashed) bonds for (a) Cr_2AlC, (b) Cr_2GaN, (c) Cr_2GaC, (d) Mn_2GaC, and (e) Cr_2GeC.

Cr_2GaN and Mn_2GaC, these compounds have been synthesized. Therefore, occupation of anti-bonding states does not immediately result in instability of the compound. However, the occupation of anti-bonding states leads to smaller integrated COHP (ICOHP) values (table 2), which indicate weaker bonds in these compounds. The M–X bonds are the strongest in Cr_2AlC, Cr_2GaC, and Cr_2GeC with ICOHP values of −1.8, −1.83, and −1.79 eV, respectively. The occupation of anti-bonding orbitals in Cr_2GaN and Mn_2GaC weakens the M–X bonds only slightly, resulting in −1.72 eV per bond for both compounds. However, it seems that the difference in the M–X bonds can be compensated by the other bonds. In Cr_2GaN, the Cr–Cr (M–M) bonds have an energy of −0.46 eV per bond and are therefore more than 0.1 eV per bond stronger than in the other synthesized compounds. In Mn_2GaC, the Mn–Ga (M–A) bonds have an energy of −0.83 eV per bond in comparison to −0.73 and −0.79 in Cr_2AlC and Cr_2GaC, respectively. Overall, the ICOHP values differ less than 0.15 eV/bond among the five synthesized compounds, leading to average ICOHP values around −0.6 eV/bond. Only Cr_2GaN stands out with an average ICOHP value of −0.55 eV/bond, as it is the only synthesized nitride.

Comparing the ICOHP values of the unsynthesized *MAX* compounds with the synthesized ones, we find six yet unsynthesized *MAX* compounds with ICOHP values similar

Table 2. Integrated COHP values in eV/bond for the 20 stable magnetic *MAX* compounds listed in table 1. The compounds in bold have been synthesized.

MAX phase	M–X	M–A	M–M	A–X	Avg.
Cr_2AlC	**−1.80**	**−0.73**	**−0.30**	**−0.08**	**−0.59**
Cr_2GaC	**−1.83**	**−0.79**	**−0.32**	**−0.09**	**−0.62**
Cr_2GaN	**−1.72**	**−0.77**	**−0.46**	**−0.07**	**−0.55**
Cr_2GeC	**−1.79**	**−0.94**	**−0.35**	**−0.10**	**−0.65**
Mn_2GaC	**−1.72**	**−0.83**	**−0.32**	**−0.08**	**−0.62**
Cr_2GeN	−1.70	−0.92	−0.42	−0.08	−0.58
Cr_2IrC	−1.77	−0.85	−0.29	−0.08	−0.62
Cr_2OsC	−1.76	−0.94	−0.26	−0.08	−0.63
Cr_2RhC	−1.80	−0.72	−0.32	−0.06	−0.59
Mn_2AlC	−1.70	−0.76	−0.29	−0.08	−0.55
Mn_2AuN	−1.40	−0.60	−0.25	−0.07	−0.51
Mn_2GaN	−1.56	−0.79	−0.38	−0.07	−0.57
Mn_2GeC	−1.71	−0.92	−0.36	−0.09	−0.64
Mn_2IrC	−1.60	−0.82	−0.18	−0.08	−0.56
Mn_2IrN	−1.41	−0.81	−0.17	−0.07	−0.52
Mn_2PdN	−1.29	−0.35	−0.19	−0.06	−0.47
Mn_2PtN	−1.40	−0.67	−0.19	−0.07	−0.54
Mn_2RhN	−1.43	−0.67	−0.18	−0.05	−0.49
Mn_2ZnC	−1.58	−0.60	−0.24	−0.07	−0.50
Mn_2ZnN	−1.42	−0.62	−0.23	−0.07	−0.49

to the synthesized compounds. Cr_2GeN, Cr_2IrC, Cr_2OsC, Cr_2RhC, Mn_2AlC, and Mn_2GeC show average ICOHP values between −0.55 and −0.64 eV/bond and therefore values in the range of the synthesized compounds. More detailed, the ICOHP values for the dominant M–X bonds are between −1.70 and −1.83 eV per bond. For all the other compounds shown in table 2, the M–X bonds are significantly weaker with −1.6 eV/bond or less. Also, the M–A, M–M, and A–X ICOHP values of the six compounds are in the same range as for the synthesized compounds, indicating similar binding states. The COHP plots (see figures 1–5 in supplementary) show that the compounds with smaller COHP values have more occupied anti-bonding states, indicating that a further stabilization may be achieved by suitable alloying.

From the discussion of the COHP and ICOHP values, we conlcude that the binding states in Cr_2GeN, Cr_2IrC, Cr_2OsC, Cr_2RhC, Mn_2AlC, and Mn_2GeC are more similar to those in the five compounds already synthesized. Three of them, Cr_2IrC, Cr_2OsC, and Cr_2RhC, are calculated to be non-magnetic, while Cr_2GeN and Mn_2AlC are calculated to be ferromagnetic and Mn_2GeC is calculated to be anti-ferromagnetic.

In [44], $(Cr,Mn)_2AlC$ compounds were synthesized, but lead to the formation of competing phases at higher Mn content in agreement with our convex hull data. The small distance to the convex hull however suggests that a stabilization of Mn_2AlC may be possible under suitable conditions.

4. Conclusion

After calculating 580 *MAX* compounds with either Cr, Mn, Fe, Co, or Ni as magnetic M-element and systematically investigating their thermodynamic, mechanical, and dynamic stability, we obtain 20 stable *MAX* compounds, including the five stoichometric magnetic *MAX* phases Cr_2AlC, Cr_2GaC, Cr_2GaN, Cr_2GeC, and Mn_2GaC that have been synthesized. We have shown that the determination and consideration of the correct magnetic ground state plays an important role for the correct evaluation of the thermodynamic stability. Considering the non-magnetic, ferromagnetic, and three anti-ferromagnetic configurations, we obtained 15 novel M_2AX compounds fulfilling all three stability criteria. Detailed analysis of the COHP and ICOHP values reveal that the five synthesized *MAX* compounds have similar binding states. Comparing the binding states of our predictions with those in the synthesized compunds, we found the most similarities for Cr_2GeN, Cr_2IrC, Cr_2OsC, Cr_2RhC, Mn_2AlC, and Mn_2GeC.

Acknowledgments

H Zhang thanks Ruslan Salikhov for insightful discussions. The authors acknowledge support from the LOEWE project RESPONSE funded by the Ministry of Higher Education, Research and the Arts (HMWK) of the Hessen state. The Lichtenberg high performance supercomputer of TU Darmstadt is gratefully acknowledged for the computational resources.

ORCID iDs

Dominik Ohmer https://orcid.org/0000-0002-7129-331X

References

[1] Barsoum M W and El-Raghy T 1996 *J. Am. Ceram. Soc.* **79** 1953–6
[2] Nowotny H 1971 *Prog. Solid State Chem.* **5** 27–70
[3] Hamm C M, Diop L V, Zhang H, Gutfleisch O and Birkel C S 2017 *Phys. Status Solidi* c **14**
[4] Mohammadzadeh R and Mohammadzadeh M 2018 *Int. J. Hydrog. Energy* **43** 7117–27
[5] Lapauw T, Lambrinou K, Cabioc'h T and Halim J 2016 *J. Eur. Ceram. Soc.* **36** 1847–53
[6] Ali M A, Hossain M M, Jahan N, Islam A K and Naqib S H 2017 *Comput. Mater. Sci.* **131** 139–45
[7] Tunca B, Lapauw T, Karakulina O M, Batuk M, Cabioc'h T, Hadermann J, Delville R, Lambrinou K and Vleugels J 2017 *Inorg. Chem.* **56** 3489–98
[8] Hamm C M, Bocarsly J D, Seward G, Kramm U I and Birkel C S 2017 *J. Mater. Chem.* C **5** 5700–8
[9] Ingason A S *et al* 2013 *Phys. Rev. Lett.* **110** 195502
[10] Mockute A, Dahlqvist M, Emmerlich J, Hultman L, Schneider J M, Persson P O Å and Rosen J 2013 *Phys. Rev.* B **87** 094113
[11] Mockute A *et al* 2014 *Phys. Status Solidi* **8** 420–3
[12] Lin S, Tong P, Wang B S, Huang Y N, Lu W J, Shao D F, Zhao B C, Song W H and Sun Y P 2013 *J. Appl. Phys.* **113** 053502
[13] Ingason A S, Petruhins A, Dahlqvist M, Magnus F, Mockute A, Alling B, Hultman L, Abrikosov I A, Persson P O Å and Rosen J 2014 *Mater. Res. Lett.* **2** 89–93
[14] Dahlqvist M, Alling B, Abrikosov I A and Rosén J 2010 *Phys. Rev.* B **81** 024111
[15] Dahlqvist M, Alling B and Rosén J 2010 *Phys. Rev.* B **81** 220102
[16] Aryal S, Sakidja R, Barsoum M W and Ching W Y 2014 *Phys. Status Solidi* b **251** 1480–97
[17] Kresse G and Hafner J 1993 *Phys. Rev.* B **48** 13115–8
[18] Kresse G and Hafner J 1994 *Phys. Rev.* B **49** 14251–69
[19] Blöchl P E 1994 *Phys. Rev.* B **50** 17953–79
[20] Singh H K H, Zhang Z, Opahle I, Ohmer D, Yao Y and Zhang H 2018 *Chem. Mater.* **30** 6983–91
[21] Opahle I, Madsen G K H and Drautz R 2012 *Phys. Chem. Chem. Phys.* **14** 16197
[22] Opahle I, Parma A, McEniry E J, Drautz R and Madsen G K H 2013 *New J. Phys.* **15** 105010
[23] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892–5
[24] Laasonen K, Car R, Lee C and Vanderbilt D 1991 *Phys. Rev.* B **43** 6796–9
[25] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 244–9
[26] Langreth D C and Mehl M J 1983 *Phys. Rev.* B **28** 1809–34
[27] Perdew J, Chevary J, Vosko S, Jackson K, Pederson M, Singh D and Fiolhais C 1992 *Phys. Rev.* B **46** 6671–87
[28] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865–8
[29] Dash D, Pandey C K, Chaudhury S and Tripathy S K 2018 *Chin. Phys.* B **27**
[30] Ohmer D, Qiang G, Opahle I, Singh H K and Zhang H 2019 *Phys. Rev. Mater.* **3** 053803
[31] Togo A and Tanaka I 2015 *Scr. Mater.* **108** 1–5
[32] Dronskowski R and Bloechl P E 1993 *J. Phys. Chem.* **97** 8617–24
[33] Jaouen M, Chartier P, Cabioc'h T, Mauchamp V, André G and Viret M 2013 *J. Am. Ceram. Soc.* **96** 3872–6
[34] Liu Z, Waki T, Tabata Y and Nakamura H 2014 *Phys. Rev.* B **89**
[35] Liu Z, Waki T, Tabata Y, Yuge K and Nakamura H 2013 *Phys. Rev.* B **88** 134401
[36] Schneider J M, Sun Z, Mertens R, Uestel F and Ahuja R 2004 *Solid State Commun.* **130** 445–9
[37] Jaouen M, Bugnet M, Jaouen N, Ohresser P, Mauchamp V, Cabioc'H T and Rogalev A 2014 *J. Phys.: Condens. Matter* **26** 6
[38] Petruhins A *et al* 2013 *Phys. Status Solidi* **7** 971–4
[39] Dahlqvist M *et al* 2016 *Phys. Rev.* B **93** 1–9
[40] Dahlqvist M and Alling B 2016 *J. Appl. Phys.* **113** 216103
[41] Ingason A S, Pálsson G K, Dahlqvist M and Rosen J 2016 *Phys. Rev.* B **94** 024416
[42] Novoselova I P *et al* 2018 *Sci. Rep.* **8** 2637
[43] Lai C C, Petruhins A, Lu J, Farle M, Hultman L, Eklund P and Rosen J 2017 *Mater. Res. Lett.* **5** 533–9
[44] Mockute A, Lu J, Moon E J, Yan M, Anasori B, May S J, Barsoum M W and Rosen J 2014 *Mater. Res. Lett.* **3** 16–22